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Experimental Protocol for Determining Absorption Cross Sections of Organic Compounds

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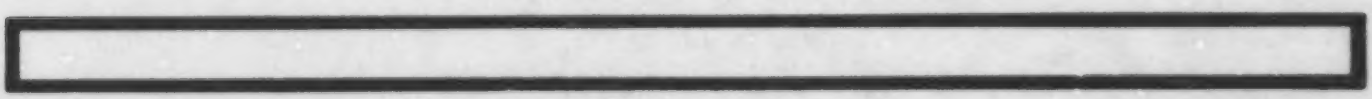

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EXPERIMENTAL PROTOCOL FOR DETERMINING ABSORPTION CROSS SECTIONS OF ORGANIC COMPOUNDS

by

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An experimental protocol for the determination of gas phase absorption cross-sections, and calculation of maximum photolysis rates, has been developed and is described in detail. Utilization of this protocol will provide a basis for evaluating the possible relative importance of one atmospheric reaction pathway (i.e., photolysis) for organic substances which may be emitted into the environment.

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SECTION I

INTRODUCTION AND BACKGROUND

Chemical compounds emitted into the troposphere through man's activities are removed or degraded by several pathways, these being gas phase reactions or wet or dry deposition. Laboratory and environmental chamber studies have shown that for the ambient atmosphere the following homogeneous gas phase removal routes are likely to be important (see, for example, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Demerjian et al. 1980, Atkinson and Lloyd 1980, and references therein):

- Photolysis, which involves absorption of light followed by isomerization or decomposition
- Reaction with ozone (O_3)
- Reaction with the hydroxyl (OH) radical

Additionally, for aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical may also be a significant loss process, especially under nighttime conditions.

Hence, in order to assess (a) the atmospheric lifetime of compounds with respect to these gas-phase removal processes and (b) the relative importance of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined for individual compounds.

In order for a chemical to be removed from the atmosphere by photolysis, it must (a) absorb light in the wavelength region applicable to the troposphere ($\lambda \gtrsim 290$ nm), and (b) having absorbed light, undergo isomerization or decomposition.

For tropospheric purposes, the wavelength region of interest is that between ~290-800 nm, the short-wavelength cut-off being determined by the transmission properties of the atmosphere (Peterson 1976, Demerjian et al. 1980), and the long-wavelength limit being set by thermochemistry, since light of wavelength $\gtrsim$ 800 nm is not of sufficient energy to break chemical bonds of ground state molecules (Calvert and Pitts 1966, Benson 1976).

Under atmospheric conditions, the photolysis rate constant, k_p, for the reaction

$$\text{compound} + h\nu \rightarrow \text{products}$$

is given by

$$k_p = \int_{\lambda=290}^{800} \sigma_\lambda \phi_\lambda J_\lambda \qquad (1)$$

where σ_λ is the absorption cross-section at the wavelength λ, ϕ_λ is the corresponding quantum yield (the fraction of molecules absorbing light which subsequently isomerize or decompose; always ≤ 1.00 for atmospheric conditions), and J_λ is the solar flux at the wavelength λ. Since the solar flux is conveniently tabulated as average values of $J_{\Delta\lambda}$ over 10 nm intervals, the integral in equation (1) can be replaced by a summation to yield

$$k_p = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} \phi_{\Delta\lambda} J_{\Delta\lambda} \qquad (2)$$

where $\sigma_{\Delta\lambda}$ and $\phi_{\Delta\lambda}$ also represent the absorption cross-section and quantum yield values averaged over 10 nm invervals.

Since $\phi_\lambda \leq 1.00$, then an upper limit to the atmospheric photolysis rate is given by

$$k_p^{max} = \Sigma_{\lambda=290}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \qquad (3)$$

and, since values of $J_{\Delta\lambda}$ are readily available (Peterson 1976), an upper limit to k_p can be calculated from a knowledge of the absorption cross-section σ_λ which can be averaged over 10 nm intervals to yield $\sigma_{\Delta\lambda}$.

The experimental procedure detailed in this protocol is designed to enable the absorption cross-sections to be determined as a function of wavelength at room temperature. Should the compound fail to exhibit a sufficient absorption cross-section or has too low a vapor pressure to yield an accurately readable absorbance, an order of magnitude approximation to its vapor phase spectrum may be acquired from solution phase data.

The actinic flux J_λ is also a function of elevation and zenith angle, which is, in turn, a function of the time of day, season and various light attenuating factors such as cloud cover, dust, etc. A compilation of $J_{\Delta\lambda}$ values, averaged over the entire day for the summer and winter solstices and the spring and fall equinoxes at 10°, 30° and 50° latitude are included here. From these data and values of $\sigma_{\Delta\lambda}$ determined using this protocol, upper limits to k_p (i.e., k_p^{max}) may be derived, yielding lower limits to the photolysis lifetimes, τ_p, since

$$\tau_p = 1/k_p \qquad (4)$$

Comparison of this calculated photolysis lifetime τ_p with those for reaction with ozone (Pitts et al. 1981a) and with the hydroxyl radical

(Pitts et al. 1981b) will then allow an assessment of the possible importance of photolysis as an atmospheric removal route. If it is of possible importance, then, since $\phi_\lambda \leq 1$, further experimental testing is necessary to determine the actual photolysis rate under atmospheric conditions.

SECTION II

GENERAL EQUIPMENT AND MATERIALS REQUIRED

The following equipment is necessary in order to determine the absorption cross-sections, σ_λ, as a function of wavelength:

- An ultraviolet-visible spectrophotometer
- Vapor and liquid absorption cells for use in the spectrophotometer
- A gas-handling system complete with vacuum pumps and pressure gauges
- Volumetric glassware for solution-phase work.

The specific requirements and recommendations for these items of equipment are discussed below.

A. Ultraviolet-Visible Spectrophotometer

The UV-visible spectrophotometer may be one constructed for a specific purpose (e.g., a long path or vacuum UV system) or be commercially available. The spectrophotometer must be able to accommodate an absorption cell of $\geq$ 10 cm in length, and be able to scan over the wavelength range 285-800 nm. Furthermore, it should have an absorbance sensitivity, at a signal/noise ratio of unity, of ~0.001. A Cary 219 UV-visible spectrophotometer or equivalent is eminently suitable.

B. Vapor and Liquid Absorption Cells

While a long path cell is preferable, most commercially available spectrophotometers will only accept cells of $\leq$ 10 cm in length. The vapor cells (Figure 1) should be constructed of Pyrex, 1 cm o.d. in diameter and 10 cm in length, and be fitted with plane parallel quartz windows on each end.

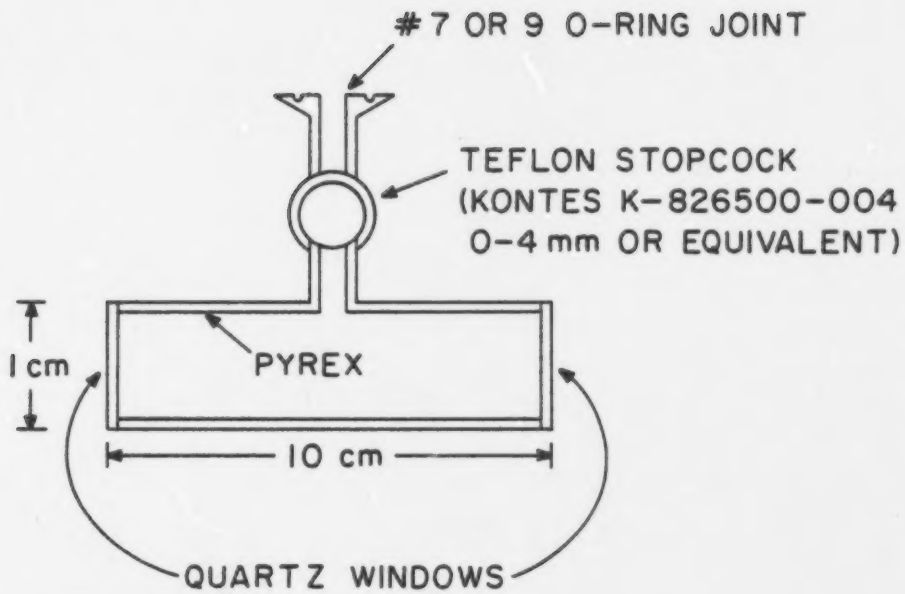


Figure 1. Gas Absorption Cell

The quartz windows are conveniently attached to the Pyrex cell by a vacuum-tight epoxy resin (e.g., Torr-Seal, sold by Varian Associates). The absorption cell should be fitted with Teflon (Teflon is a registered tradename of E.I. du Pont de Nemours and Co., Inc.) stopcocks and "o"-ring joints. The "o"-ring joints (#7 or #9, Kontes or Ace Glass, are satisfactory) must obviously match those on the vacuum rack. The "o"-rings must be of Viton and be inspected frequently for signs of wear and irregularities, which could result in leaks. The use of stopcock grease is not required and should be avoided, since many organics are absorbed into greases.

A "matched" reference cell is useful but not required for short path work. However, for precise results the reference cell should be similar to the sample cell. Small spectral differences between cells can be compensated for by obtaining blank spectra prior to filling.

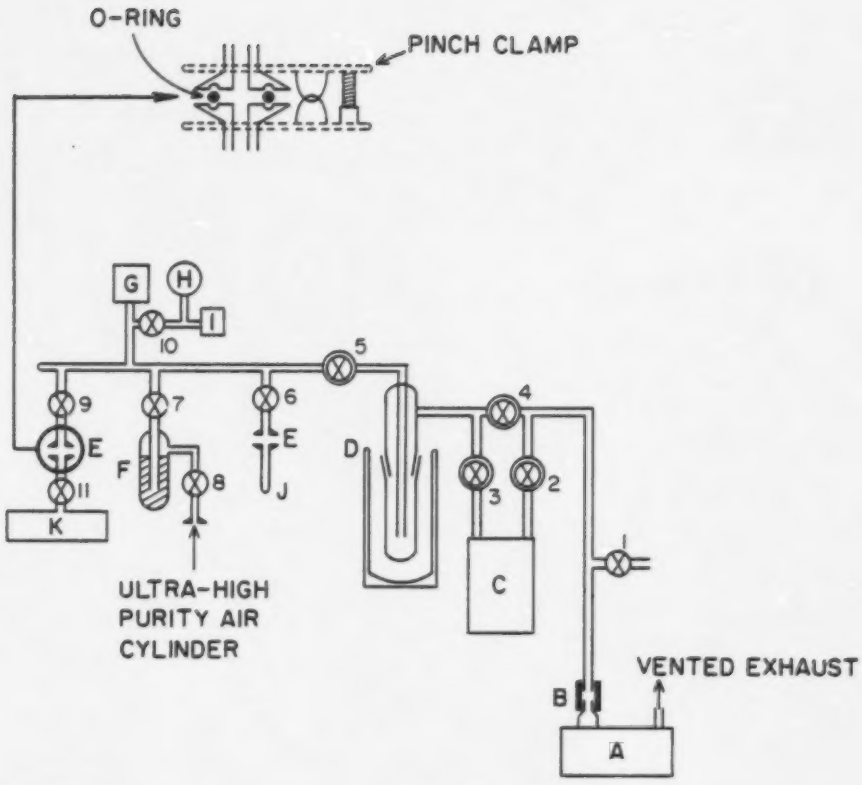
A matched pair of liquid cells is similarly helpful but not required. They should be 10 cm in length and have a ground glass or Teflon stopper. The pathlength of the cells must again be accurately determined (e.g., by calipers) to better than $\pm$ 0.1 cm.

C. Vacuum Gas-Handling System

A suitable gas-handling system is shown diagramatically in Figure 2. Such a system should preferably be constructed from Pyrex, since the use of other materials, such as various metals, can lead to wall adsorption problems. The components of such a gas handling system are discussed below.

1. Vacuum Pumping System

Two pumps, working in tandem, are necesary to provide good vacuum, i.e., pressures $\lesssim 10^{-5}$ torr. The forepump (A) must be capable of achieving pressures $\lesssim$ 0.05 torr. A rotary pump such as a Welch Model 1402 Duo-Seal or



A ROTARY PUMP
B RUBBER TUBING (THICK WALLED)
C DIFFUSION PUMP
D TRAP AT LIQUID NITROGEN TEMPERATURE
E #7 OR 9 O-RING JOINTS
F MOLECULAR SIEVE 4A TRAP
G CAPACITANCE MANOMETER
H THERMOCOUPLE GAUGE
I IONIZATION GAUGE
J LIQUID RESERVOIR
K GAS ABSORPTION CELL

⊗ 0-4 OR 0-5 mm STOPCOCKS

⊗ 0-8 OR 0-10 mm STOPCOCKS

Figure 2. Schematic of Gas Handling Vacuum Rack

equivalent is recommended for this purpose. The forepump is attached to the rest of the vacuum system by heavy-walled rubber vacuum tubing (B), which also serves to damp-out transmission of vibrations to the vacuum line. The exhaust from this pump should be vented into a hood. The second, and high-vacuum, pump required is a multistage oil diffusion pump (C), a CVC (Consolidated Vacuum Corporation) VMF-10 or VMF-20 or equivalent being suitable. The working fluid should be a silicone oil (e.g., Dow-Corning D.C. 702 or D.C. 703) since they are less susceptible to destructive oxidation should the system be inadvertently vented to air while the diffusion pump is still hot. The diffusion pump fluid must have a room temperature vapor pressure of $\lesssim 10^{-6}$ torr.

The pumping system must be equipped with a trap (D) cooled by liquid nitrogen (i.e., at 77°K), to reduce pump oil contamination and backstreaming. The cone and socket portions of this trap (Figure 2) may be conveniently sealed using Apiezon W wax (which requires gentle heating to apply).

2. Vacuum Rack

A suitable assembly of the vacuum rack is as shown in Figure 2. The stopcocks should be of Teflon with Viton "o"-rings such as the Kontes #K-826500 or K-826510 series. The "o"-ring joints (#7 or #9 size are suitable) must be chosen to be compatible with those on the gas absorption cell. These "o"-ring joints are clamped by, preferably, pinch clamps with a screw lock device (Thomas #18A, available from VWR Scientific, Inc., for example).

3. Pressure Gauges

Two or, preferably three, pressure gauges are required:

(a) An ionization gauge to measure high vacuum, i.e., pressures $\lesssim 10^{-3}$ torr, to verify that the vacuum system is operating correctly and that there are no leaks.

(b) If available, a thermocouple gauge is desirable to monitor, on a semi-quantitative basis, pressures in the range ~10^{-3} to 1 torr. This gauge is used to monitor the pressures in the gas handling system prior to turning on either the diffusion pump (which requires $\lesssim$ 0.1 torr) or the ionization gauge. A convenient and totally satisfactory pressure monitoring system which includes both these gauges is the CVC Products, Inc. Model GIC-300A ionization gauge with associated thermocouples, or equivalent.

(c) The third pressure gauge is needed to accurately monitor pressures of the test compound and diluent in the range ~0.01 to 760 torr. It is recommended that for this purpose a capacitance manometer be used, such as an MKS Baratron 310 BHS-1000 with an associated 170-6C electronics unit and a digital readout (this particular system has an accurately useable range of < 0.1 to 1000 torr). While these vacuum gauges exhibit a slow zero drift, they can be readily rezeroed using the ionization gauge, i.e., when the ionization gauge reads $\lesssim 10^{-3}$ torr.

D. Volumetric Glassware for Solution Phase Work

For the preparation of solutions of known concentration, a series of conveniently sized analytical volumetric flasks, pipettes and/or syringes are required.

All glassware should be cleaned in soap (e.g., trisodium phosphate or an organic sulfonate) and water, rinsed with several portions of distilled water and allowed to dry at room temperature. Oven drying must be avoided as it tends to expand glass. Cleanliness may be checked by filling with

water; if the meniscus pulls away from areas of the glass, leaving drops and dry spots, further cleaning using a chromic acid solution is required.

SECTION III

EXPERIMENTAL PROTOCOL

A. Operation of Gas Handling System

The following describes briefly the typical operation of the vacuum gas handling system.

(1) With all stopcocks closed, switch on rotary pump (A), then open stopcock 4 and place a Dewar of liquid nitrogen around trap D.

(2) Open stopcock 10 and monitor the pressure using the thermocouple gauge (H). If the pressure is $\gtrsim$ 0.1 torr, then open stopcock 5. When the pressure as read by the thermocouple gauge (H) is $\lesssim$ 0.1 torr, turn on the diffusion pump (C), open stopcocks 2 and 3 and close 4. When the diffusion pump has reached operating temperature, the pressure in the vacuum manifold should be $\lesssim 10^{-5}$ torr as read by the ionization gauge (I). At this point the capacitance manometer (G) can be zeroed. The ionization gauge (I) should only be used when, as indicated by the thermocouple gauge (H), the pressure is $\leq 10^{-3}$ torr.

(3) The gas absorption cell (K) can now be evacuated by opening stopcocks 9 and 11. If the cell is at a substantial pressure, then prior to opening these stopcocks, the diffusion pump should be bypassed by opening stopcock 4 and closing 2 and 3 (the diffusion pump should not, if avoidable, be exposed to pressures $\gtrsim$ 0.1 torr to avoid degradation of the pump oil). Similarly, the trap (F) filled with activated (carried out by heating the trap to ~150°C for 1-2 hours under vacuum) Linde Molecular Sieve 4A and the

reservoir (J) can be evacuated in a similar manner. It should be pointed out that it is good practice, when the gas phase spectra have been obtained, to evacuate the gas absorption cell (K) and the trap (F) prior to shutting down the gas handling system. The gas handling system can be shut down by the following procedure: (a) closing stopcocks 5 to 11, (b) switching off the diffusion pump, (c) when the diffusion pump is cool, closing stopcocks 2 and 3 and opening 4, (d) removing the Dewar from trap (D) and allowing it to warm up, (e) then closing stopcock 4 and switching off the rotary pump and (f) opening stopcock 1 to admit air to the rotary pump, thus preventing suck-back of the rotary pump oil. With this procedure, the vacuum manifold, the trap D and the diffusion pump are left under vacuum. The liquid reservoir (J) should also be cleaned with methanol or dichloromethane as solvent and dried, ready for use.

If the vacuum system, including the gas absorption cell (i.e., all stopcocks open except stopcocks 1, 4, 6 and 7) does not pump down to $< 10^{-4}$ torr, then either a leak or contaminant offgassing problems are present. Closing stopcocks 11, then 9, will give indications as to the region of the problem, i.e., if on closing stopcock 9 the pressure drops then there may be a leak around the "o"-ring joint on the gas absorption cell, which then should be replaced. If, however, the pressure drops on closing stopcock 11 (with 9 open) then either the gas absorption cell has a leak or test compound off-gassing from previous runs is occurring. Leaks can be checked using a tesla coil.

Offgassing can normally be reduced by prolonged pumping, cleaning the cell with methanol and/or dichloromethane and/or distilled water, and pumping or by replacing stopcock 11 (which may have absorbed the compound to

some extent). Such "maintenance" procedures should be routinely observed and carried out on all portions of the vacuum gas handling system. This includes changing the rotary pump oil at frequent intervals.

B. Preparation of the Test Compound Sample

If the test compound is gaseous, the container should be attached via an "o"-ring joint to the position of the liquid reservior, and the intervening dead-volume evacuated.

If the test compound is liquid, then several cm^3 of the liquid are placed into the liquid reservoir (J), which is conveniently an "o"-ring joint (#7 or #9) with the end glass sealed off. The sample is then cooled by immersing the reservoir tube (J) in liquid nitrogen, and pumped on by opening stopcock 6. The compound is then degassed by freezing in a liquid nitrogen bath, evacuating to approximately 10^{-4} torr, sealing off the reservoir and allowing it to thaw. This process should be repeated three or more times and until the evolution of gas bubbles upon thawing ceases.

C. Introduction of Test Compound into the Gas Absorption Cell

For introduction of the compound into the gas absorption cell, stopcocks 5, 7 and 10 should be closed, with 9 and 11 open. If the compound is gaseous, then stopcock 6 should be open to the gas container and the valve on the container gradually opened to admit the gas into the gas handling manifold and gas absorption cell until the required pressure, as read by the capacitance manometer, is attained. The gas container valve should then be closed, and stopcock 6 closed.

For a liquid compound in the reservoir (J), which has been degassed and is at liquid nitrogen temperature, the liquid nitrogen Dewar should be removed, and stopcock 6 opened. The cold liquid in the reservoir (J) is allowed to

warm up until the required pressure, as read by the capacitance manometer, is attained. Stopcock 6 should then be closed and the liquid nitrogen Dewar replaced around the reservoir (J).

In both cases, after ~1-5 minutes for equilibration, the pressure in the gas absorption cell is monitored by the capacitance manometer (G) and stopcock 11 closed. A possible problem concerns adsorption of the test compound onto the walls of the gas handling system, resulting in a steadily decreasing pressure after the reservoir J is isolated by closing stopcock 6. Such adsorption problems are generally worse if metal surfaces are exposed to the test compound. For this reason, we have recommended the use of a capacitance manometer, with its small exposed surface, compared to, for instance, the Wallace and Tiernan series of absolute pressure gauges. If significant adsorption is occurring, i.e., the pressure of the test compound decreases continuously, the pressure should be noted at the time stopcock 11 is closed. The time between closing stopcock 11 and the taking of the spectrum should also be noted, and spectra should be retaken at various time intervals (say every 15 minutes) to determine the extent, if any, of wall adsorption problems in the gas absorption cell leading to decreasing absorbances. If so, the absorbances should be linearly corrected back to the time that stopcock 11 was closed and the test compound pressure recorded.

The gas handling manifold is then evacuated (i.e., stopcocks 6, 8 and 11 closed; 5, 7 and 9 open), including the trap (F). Stopcock 5 is then closed and ultra-high purity air from a cylinder admitted into the gas handling manifold via stopcock 8 through the the trap containing Molecular Sieve 4A. When the manifold is at atmospheric pressure, stopcock 11 is briefly opened to

pressure the gas absorption cell to atmospheric, then closed. The gas absorption cell should be covered to avoid photolysis.

D. Obtaining a Spectrum

The UV-visible spectrum is then measured relative to a matched cell filled with the ultra-high purity air from the same cylinder similarly passed through the trap (F) containing Molecular Sieve. The spectrum should be measured from 285-825 nm using minimum slit openings. This procedure is repeated at at least two other pressures differing by factors of between two and 10 (e.g., 1, 5 and 20 torr), depending on the strength of the absorption and the sensitivity and stability of the spectrophotometer. Since many compounds do not absorb at the higher wavelengths, it is acceptable to begin the scan at ~50 nm above the beginning of the lowest energy absorption.

Immediately prior to and after each set of runs, a blank spectrum should be obtained. The UV cell should be evacuated to 10^{-5} torr and filled with the ultra-high purity air dried through Molecular Sieve 4A. The cell is then placed in the spectrophotometer and a spectrum obtained relative to the reference cell, using the same sources, scale and slit widths as are to be used for sample spectra.

The concentration of the gas sample is given by:

$$\text{Concentration} = [\text{test compound pressure (torr)}] \times 9.6579 \times 10^{18}/T(^{o}K) \quad \text{molecule cm}^{-3} \qquad (5)$$

where T is room temperature, which should be routinely monitored using a thermometer.

E. Procedure for Obtaining Solution Phase Absorption Spectra

If the properties of the compound (e.g., small absorption cross sections, low vapor pressure) are such that the maximum absorbance obtainable is one-tenth of the most sensitive spectrophotometer scale or less (i.e., $\leq$ 0.001

absorbance), a solution-phase study should be undertaken. The most sensitive scale may be limited by inherent spectrophotometer noise. For example, a given spectrophotometer's most sensitive scale is 0.00 to 0.10 absorbance units. Therefore, a compound for which the product of its maximum cross section and its concentration is less than 0.001 (10 cm cell) could not be analyzed in the vapor phase with this particular spectrophotometer. While not capable of yielding an accurate value for σ_λ, solution phase results are reproducible and yield an order-of-magnitude approximation.

1. Choice of Solvent

There are two requirements for the solvent. It must be transparent in the actinic region ($\lambda \gtrsim 290$ nm) and the test compound must be sufficiently soluble in it. A partial list of solvents satisfying the first of the criteria is included below:

	Short Wavelength Cutoff (nm)
Carbon tetrachloride	265
Chloroform	240
1,4-Dioxane	220
n-Hexane	215
Acetonitrile	210
Cyclohexane	205

The solvents other than carbon tetrachloride are preferred. In general, solvents such as water, organic acids and alcohols (e.g., methanol, ethanol) should be avoided because of their greater ability to perturb absorption spectra. Solvent effects exist, however, and will affect values for k_p. The wavelength and cross sections of vapor-phase absorption maxima are altered by dissolution.

The solvents used shall be spectrophotometric grade. Care should be taken to ensure that the same lot is used thoughout a series of solutions to avoid the minor variations in contamination found in different solvent lots.

2. Preparation of Liquid Phase Sample

The compound quality and purity shall be the same as that to be marketed. If light sensitivity is suspected, all manipulation involving the compound shall be performed in the dark or under photographic safelights.

Proper precautions for personal safety shall be exercised. Gloves and goggles shall be worn when they are deemed necessary. Manipulations of volatile toxic substances shall be performed in a vented hood. Explosive compounds shall be manipulated in a hood behind a blast shield.

At least three solutions shall be prepared using each of two solvents. The sample is added by a calibrated pipette or syringe to a flask half-filled with solvent. It is immediately stoppered and shaken to initiate mixing. The stopper is then removed, the solution diluted to the mark and the stopper replaced. Adequate mixing is best accomplished by a series of at least 75 inversion/shaking cycles. The solutions shall be prepared so as to cover as large a concentration range as possible, but not to exceed approximately 10% v/v, so as to maintain, as far as possible, a dilute solution.

3. Obtaining a Spectrum

Immediately prior to and after each set of runs, a blank spectrum should be obtained. The reference and sample cells of a matched pair of quartz windowed 10 cm cells are filled with solvent and stoppered with a glass or Teflon stopper. They are then placed in the spectrophotometer and a spectrum recorded over the region 800-285 nm. It is important that the

sources, slit widths and sensitivity be identical to those used in obtaining sample spectra. A similar blank should be obtained after the completion of sample runs as a check of instrument stability.

The solutions shall be run in the following order: blank, least-to most-concentrated solution, blank. After the initial blank, the solvent is emptied from the sample cell and several milliliters of the least concentrated solution are added as a rinse. Several small aliquots of this kind are required to adequately eliminate traces of the previous sample. After approximately three rinsings, the cell may be filled and a spectrum obtained. The second and third solutions are similarly used to rinse the cell prior to obtaining their spectra. The cell must be cleaned more thoroughly before the second blank can be obtained. Several cycles of two rinsings and evacuation by a water aspirator should be adequate. Insufficient cleaning may be detected by the appearance of absorption due to the compound in the blank spectrum.

4. Concentration

The concentration of the sample is given by

$$\text{Concentration} = \frac{V_s \times \rho}{\text{M.W.} \times V_d} \times 6.02 \times 10^{20} \text{ molecule cm}^{-3} \qquad (6)$$

where V_s is the volume of sample delivered into V_d, the dilution volume, ρ is the compound's density and M.W. its molecular weight (grams).

F. Calculation of the Maximum Photolysis Rate Constant k_p^{max}

Following the recording of the absorption spectrum over the solar region, the maximum photolysis rate constant (i.e., assuming a decomposition quantum yield of unity) is calculated from the blank and sample spectra as follows:

1. The Blank Spectrum

The blank spectrum, with both the reference and sample cells filled with either dried ultra-high purity air or solvent, is used to correct the sample spectra for absorbance due to small spectral differences between the cells. A matched pair of cells should require minimal correction. The absorbance between the sample cell in the presence and absence of the test compound, using the reference cell as a "standard", is then the true corrected absorbance of that concentration of the test compound.

The absorbance of the blank spectrum, with both the reference and sample cells filled with either dried ultra-high purity air or solvent, should be referenced to a zero value at any arbitrary wavelength, and this is conveniently the low wavelength point (i.e., λ = 285 nm). In any case the "zero wavelength" must be the same for all blank and sample runs.

Then at any wavelength λ, the corrected absorbance of the sample containing the test compound A^{corr}_{sample} is given by

$$A^{corr}_{\lambda sample} = A^{observed}_{\lambda sample} - A_{\lambda blank} \qquad (7)$$

and, of course, A_{blank} may be positive or negative, leading to negative or positive corrections to the observed sample absorbances $A^{observed}_{sample}$.

Since with any reasonably well matched pair of absorption cells the correction, i.e., A_{blank}, is small, it will almost always be sufficient to tabulate the average value of A_{blank} over 10 nm wavelength intervals 285-295, etc.

This, with 10 nm wavelength averaged sample absorbances, leads to

$$A^{corr}_{\Delta\lambda sample} = A^{observed}_{\Delta\lambda sample} - A_{\Delta\lambda blank} \qquad (8)$$

2. Determination of Wavelength-Averaged Sample Absorbances

There are at least three nondestructive methods of determining an average absorbance over a specific wavelength region.

(1) Estimation

(2) Square counting

(3) Planimetry.

The technique of cutting and weighing the spectrum is destructive and liable to significant errors due to differing water contents of differing portions of the paper on which the spectrum is obtained.

For many spectra, estimating an average absorbance over a small wavelength range is sufficient to yield accurate values. While convenient, however, this is not the method of choice for spectra exhibiting rapidly increasing and decreasing absorptions and complex fine structure.

The other two methods require the integration of a definite region (in A x nm) followed by division by the width (in nm) to arrive at the average absorbance.

The counting of squares is a useful and, for most spectra, adequate means of interval integration. For example, a 10 nm interval, from 285-295 nm, with a sensitivity of one vertical unit = 0.001A (one horizontal unit/nm) contained 732 squares. Therefore, the average absorbance is 0.0732A. For a gently changing spectrum, a relatively large error, e.g., one square, corresponds to only a 0.14% error in A over this interval. However, a spectrum with a complicated fine structure may be difficult to analyze in this manner.

Probably the most accurate method for the area determinations, and the one recommended here, involves the use of a compensating polar

planimeter. This device measures the areas of plane figures of any form. The area of a figure is related to the distance a measuring wheel has revolved after a tracer point is run around the figure's periphery. Planimeters are marketed by a number of companies (e.g., Keuffel & Esser, Bruning) and those with an adjustable tracer arm are preferred as their sensitivity can be maximized by adjustment of the tracer arm to its smallest length. Each spectrum must be calibrated to adjust for slight differences in grid size. A convenient number of squares is traced and the planimeter vernier reading noted. A second and third tracing should be performed and a vernier unit (v.u.) per square correlation established.

Each interval shall be traced at least three times to arrive at an average v.u. reading for the interval. The v.u. reading is then converted to the number of squares, which in turn is easily converted to a value for the average absorption.

The relative accuracies of the methods presented here will vary depending upon the kind of spectrum, the inherent accuracy of the method and the person performing the integration. The methods have been presented in the estimated order of accuracy. A planimeter, with careful measurement, can be expected to yield an accuracy of 0.3% with figures larger than 65 cm^2. The accuracy can be expected to be somewhat lower when measuring smaller spectral areas.

3. Calculation of the Maximum Photolysis Rate k_p^{max}

The average absorbances over each of the intervals for which $J_{\Delta\lambda}$ values are listed (see Tables 1, 2 and 3) are tabulated. Photochemical cross sections are then determined from the Beer-Lambert Law:

$$\sigma_{\Delta\lambda} = A_{\Delta\lambda}/lC \qquad (9)$$

where $\sigma_{\Delta\lambda}$ is the wavelength averaged cross section in cm^2 $molecule^{-1}$, l is the cell pathlength in cm, C is the concentration of absorbing species in molecule cm^{-3} and $A_{\Delta\lambda}$ is the wavelength averaged absorbance (in logarithm to the base e units). If the absorbance is given in base 10 units, then it must be multiplied by 2.3026 to convert to base e units. For some compounds, especially those exhibiting sharp absorption maxima (e.g., benzene, toluene), equation (9), i.e., the Beer-Lambert law, is not obeyed and σ_λ decreases with increasing concentration C (or absorbance A), as shown in Figure 3 for the case of toluene. In these cases, the limiting values of σ_λ at low concentration (or absorbance) should be used for the calculations of k_p^{max}, and, as shown from Figure 3, deviations from the Beer-Lambert law generally occur at higher concentrations, so extrapolation to low concentration values of σ_λ is readily carried out.

The cross sections $\sigma_{\Delta\lambda}$ are then combined with the solar intensities for 10°, 30° and 50°N latitude from Tables 1, 2 and 3, respectively (Hendry and Kenley 1979, from the ground level compilations of Peterson 1976). These day-averaged $J_{\Delta\lambda}$ values will yield a day-averaged maximum photolysis rate constant, k_p^{max} of:

$$k_p^{max} = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda}$$

Since for many photochemical processes, the quantum efficiency is less than unity, k_p^{max} will most often represent an upper limit to the true photolysis rate constant k_p.

Solution phase $\sigma_{\Delta\lambda}$ values should also be averaged and the results for each solvent reported, along with the resulting values of k_p^{max}.

TABLE 1. $J_{\Delta\lambda}$ (photons cm^{-2} day^{-1}) VALUES AT 10°N LATITUDE[a]

Wavelength Range, nm	Solstice				Equinox		Season Average			
	Summer		Winter				Spring/Summer		Fall/Winter	
285-295	0		0		0		0		0	
295-305	6.39	17	3.31	17	6.38	17	6.63	17	4.6	17
305-315	9.701	18	6.679	18	9.522	18	9.815	18	7.91	18
315-325	2.451	19	1.852	19	2.386	19	2.457	19	2.685	19
325335	4.474	19	3.518	19	4.341	19	4.468	20	3.877	19
335-345	4.945	19	3.957	19	4.789	19	4.828	19	4.321	19
345-355	5.666	19	4.605	19	5.479	19	5.638	19	4.925	19
355-365	5.85	19	4.758	19	5.656	19	5.820	19	4.925	19
365-375	7.301	19	5.976	19	7.655	19	7.226	19	6.357	19
375-385	7.157	19	5.891	19	6.913	19	7.125	19	6.343	19
385-395	7.329	19	6.065	19	7.075	19	7.278	19	6.663	19
395-405	1.004	20	8.341	19	9.687	19	9.966	19	8.917	19
405-415	1.273	26	1.063	20	1.23	20	1.265	20	1.135	20
415-525	1.331	20	1.114	20	1.283	20	1.320	20	1.187	20
425-435	1.349	20	1.133	20	1.30	20	1.338	20	1.205	20
435-445	1.491	20	1.256	20	1.436	20	1.478	20	1.339	20
445-455	1.718	20	1.449	20	1.655	20	1.702	20	1.538	20
455-465	1.857	20	1.568	20	1.789	20	1.840	20	1.664	26
465-475	1.914	20	1.619	20	1.843	20	1.896	20	1.716	20
475-485	1.941	20	1.645	20	1.869	20	1.922	20	1.742	20
485-495	1.945	20	1.652	20	1.873	20	1.926	20	1.747	20
495-515	3.970	20	3.370	20	3.823	20	3.932	20	3.565	20
515-535	4.013	20	3.41	20	3.863	20	3.974	20	3.605	20
535-555	3.995	20	3.398	20	3.846	20	3.956	20	3.591	20
555-575	4.053	20	3.446	20	3.902	20	4.014	20	3.692	20
575-595	4.197	20	3.573	20	4.04	20	3.659	20	3.774	20
595-635	8.529	20	7.235	20	8.211	20	8.446	20	7.652	20
635-675	8.976	20	7.658	20	8.637	20	8.884	20	8.077	20
675-715	9.077	20	7.778	20	8.732	20	8.961	20	8.186	20
715-755	8.744	20	7.514	20	8.41	20	8.65	20	7.897	20
755-795	8.460	20	7.287	20	8.135	20	8.367	20	7.648	20

[a]Second number in column is the power of ten by which the first number is multiplied.

TABLE 2. $J_{\Delta\lambda}$ (photons cm^{-2} day^{-1}) VALUES AT 30°N LATITUDE

Wavelength Range, nm	Solstice				Equinox		Season Average			
	Summer		Winter				Spring/Summer		Fall/Winter	
285-295	1.0	16	0	16	0	17	1.18	15	0	17
295-305	7.40	17	6.80	16	3.98	17	6.24	17	1.78	17
305-315	1.09	19	2.83	18	7.49	18	9.77	18	4.60	18
315-325	2.74	19	1.00	19	2.03	19	2.50	19	1.41	19
325-345	4.98	19	2.11	19	3.82	19	4.58	19	2.79	19
335-345	5.49	19	2.48	19	4.28	19	5.07	19	3.20	19
345-355	6.28	19	3.11	19	4.96	19	5.82	19	3.68	19
355-365	6.49	19	3.10	19	5.13	19	6.01	19	3.92	19
365-375	8.09	19	3.95	19	6.43	19	7.51	19	4.96	19
375-385	7.93	19	3.95	19	6.33	19	7.36	19	4.92	19
385-395	8.12	19	4.12	19	6.51	19	7.55	19	5.09	19
395-405	1.11	20	5.72	19	8.94	19	1.03	20	7.04	19
405-415	1.41	20	7.36	19	1.14	20	1.31	20	8.64	19
415-425	1.47	20	7.80	19	1.19	20	1.37	20	9.37	19
425-435	1.49	20	7.99	19	1.21	20	1.39	20	9.67	19
435-445	1.65	20	8.93	19	1.34	20	1.54	20	1.08	20
445-455	1.90	20	1.04	20	1.55	20	2.77	20	1.25	20
455-465	2.05	20	1.13	20	1.67	20	1.92	20	1.35	20
465-475	2.12	20	1.17	20	1.73	20	1.98	20	1.40	20
475-485	2.15	20	1.19	20	1.75	20	1.01	20	1.42	20
485-495	2.15	20	1.20	20	1.76	20	2.01	20	1.43	20
495-515	4.39	20	2.45	20	3.59	20	4.10	20	2.92	20
515-535	4.44	20	2.49	20	3.63	20	4.15	20	2.96	20
535-555	4.42	20	2.49	20	3.62	20	4.13	20	2.95	20
555-575	4.48	20	2.52	20	3.67	20	4.19	20	2.99	20
575-595	4.64	20	2.62	20	3.80	20	4.34	20	3.11	20
595-635	9.44	20	5.39	20	7.70	20	8.81	20	6.34	20
635-675	9.92	20	5.72	20	8.15	20	9.28	20	6.72	20
675-715	1.00	21	5.85	20	8.27	20	9.39	20	6.84	20
715-755	9.67	20	5.70	20	7.98	20	9.05	20	6.64	20
755-795	9.35	20	5.37	20	7.74	20	8.76	20	6.46	20

TABLE 3. $J_{\Delta\lambda}$ (photons cm^{-2} day^{-1}) VALUES AT 50°N LATITUDE

Wavelength Range, nm	Solstice				Equinox		Season Average			
	Summer		Winter				Spring/Summer		Fall/Winter	
285-295	0		0		0		0		0	
295-305	5.7	17	6.0	14	1.12	17	3.763	17	2.55	16
305-315	1.005	19	2.981	17	3.945	18	7.724	18	1.398	18
315-325	2.680	19	1.857	18	1.317	19	2.173	19	5.699	18
325-335	5.0	19	5.429	18	2.714	19	4.162	19	1.314	19
335-345	5.577	19	7.118	18	3.163	19	4.700	19	1.597	19
345-355	6.446	19	8.513	19	3.86	19	5.495	19	1.984	19
355-365	6.659	19	9.536	18	3.923	19	5.670	19	2.057	19
365-375	8.341	19	1.248	19	4.985	19	7.130	19	2.648	19
375-385	8.204	19	1.279	19	4.967	19	7.038	19	2.646	19
385-395	8.427	19	1.070	19	5.165	19	7.255	19	2.816	19
395-405	1.157	20	1.951	19	7.161	19	9.987	19	3.949	19
405-415	1.472	20	2.569	19	9.194	19	1.274	20	5.132	19
415-425	1.540	20	2.792	19	9.715	19	1.337	20	5.478	19
425-435	1.564	20	2.915	19	9.938	19	1.361	20	5.652	19
435-445	1.732	20	3.326	19	1.109	20	1.510	20	6.366	19
445-455	1.996	20	3.91	19	1.283	20	1.743	20	7.413	19
455-465	2.159	20	4.30	19	1.392	20	1.886	20	8.087	19
465-475	2.227	20	4.533	19	1.443	20	1.948	20	8.444	19
475-485	2.261	20	4.685	19	1.471	20	1.981	20	8.639	19
485-495	2.268	20	4.769	19	1.483	20	1.983	20	8.758	19
495-515	4.629	20	9.789	19	3.026	20	4.060	20	1.791	20
515-535	4.682	20	1.001	20	3.069	20	4.109	20	1.823	20
535-555	4.664	20	1.002	20	3.062	20	4.095	20	1.822	20
555-575	4.732	20	1.014	20	3.104	20	4.153	20	1.845	20
575-595	4.903	20	1.063	20	3.228	20	4.308	20	1.926	20
595-635	9.935	20	2.227	20	6.631	20	8.749	20	3.983	20
635-675	1.048	21	2.463	20	7.015	20	9.253	20	3.428	20
675-715	1.061	21	2.610	20	7.165	20	9.40	20	4.431	20
715-755	1.023	21	2.644	20	6.977	20	9.089	20	4.370	20
755-795	9.902	20	2.648	20	6.809	20	8.821	20	4.311	20

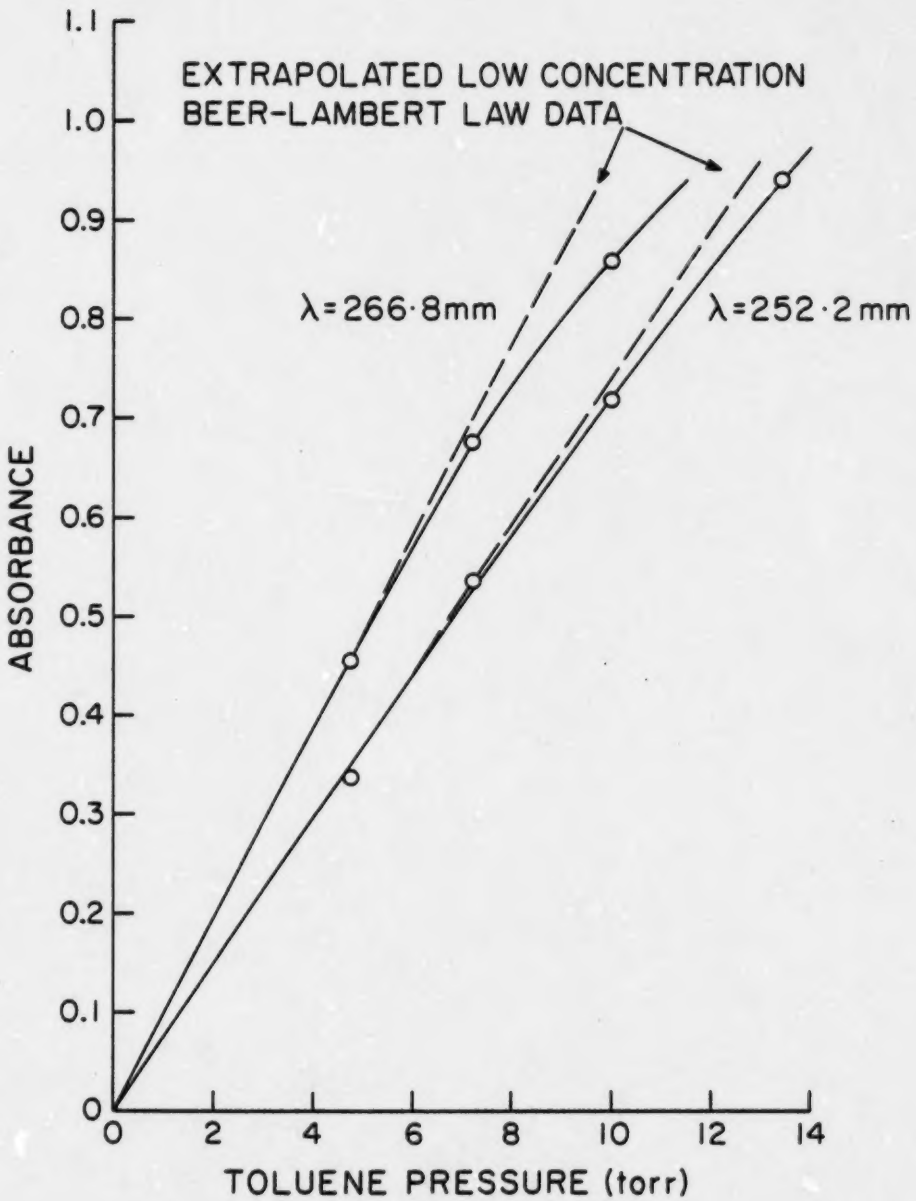


Figure 3. Plot of Absorbance Versus Toluene Pressure for Two Peak Wavelengths

4. Sample Calculation

A vapor phase absorption spectrum of acrolein (CH_2=CHCHO) as determined using the above discussed experimental protocol is reproduced in Figure 4. The gas absorption cell had a length of l = 9.98 cm and contained 6.52×10^{16} molecule cm^{-3} of acrolein. The spectrum was obtained relative to a matched reference cell on a Cary 219 spectrophotometer (0-0.1 A sensitivity range).

A compensating polar planimeter was used to integrate each 10 nm interval centered around 290, 300, 310, 320 nm, etc. A blank spectrum was obtained prior to the sample spectrum. One square on this chart was found to be equal to 0.148 vernier units.

Table 4 shows the calculation of k_p^{max} for this particular spectrum for the $J_{\Delta\lambda}$ values listed in Table 2 (30° N latitude, summer solstice).

A sample calculation is included below for the interval 345-355 nm. For convenience, an area of 100 squares (Area A on Figure 4) was excluded from integration by the planimeter as it lay below the absorbance line. The average vernier reading for the remaining area was 7.2.

Hence,

$$\frac{7.2 \text{ v.u.}}{0.148 \text{ v.u./square}} = 49 \text{ squares}$$

and the total area under the measured spectrum, $345 \leq \lambda \leq 355$ nm = 149 squares. The number of squares is then converted to absorbance units (A) averaged over the 10 nm interval by

$$\frac{(149 \text{ squares})(0.001 \text{ A/square})}{10} = 0.0149 \text{ absorbance units}$$

From the blank spectrum, the baseline over the interval 345-355 nm, was

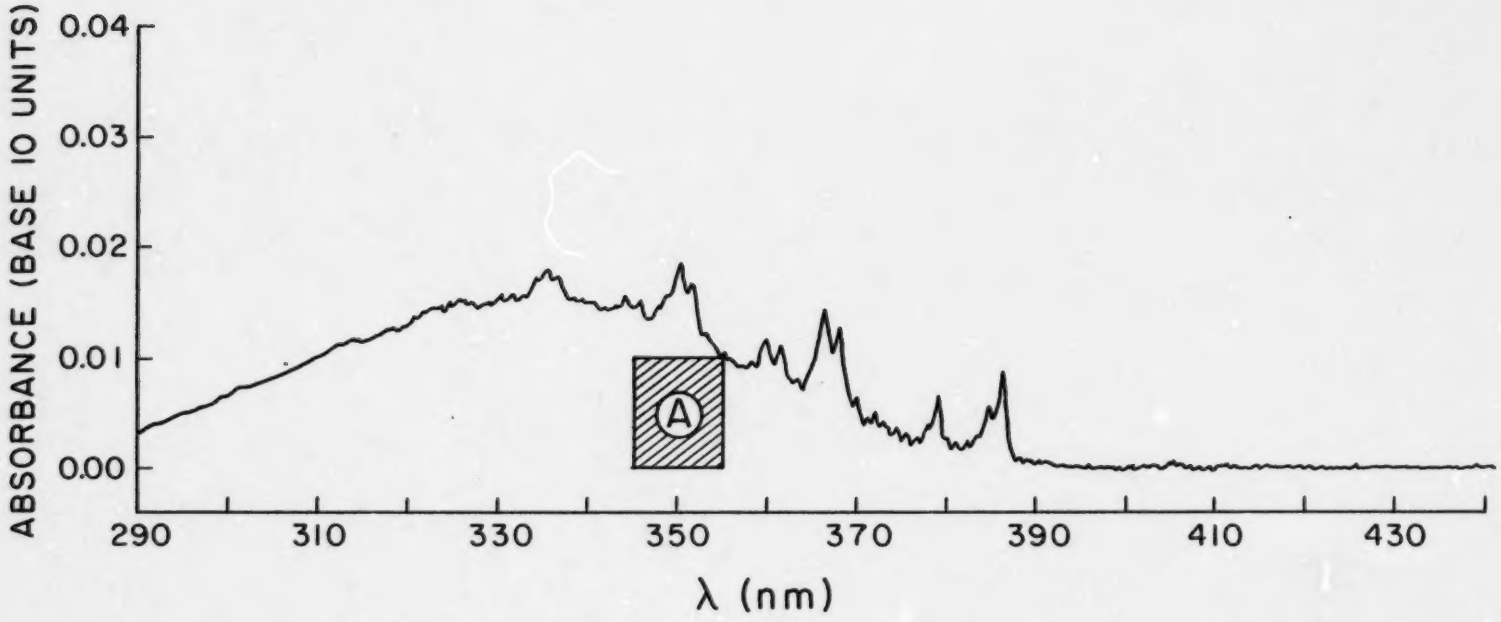


Figure 4. Gas Phase Absorption Spectrum of Acrolein

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Table 4. CALCULATION OF k_p^{max} FOR ACROLEIN VAPOR*
DAY RATE AT 30°N ON SUMMER SOLSTICE

Wavelength Interval (nm)	Average Absorbance	Average Cross Section $\sigma_{\Delta\lambda}$ (base e) cm^{-2} $molecule^{-1}$	$J_{\Delta\lambda}$ photons cm^{-2} day^{-1}	$J_{\Delta\lambda}\sigma_{\Delta\lambda}$	$\Sigma J_{\Delta\lambda}\sigma_{\Delta\lambda}$
285-295	0.0085	1.31×10^{-20}	1.0×10^{16}	0.00013	0.00013
295-305	0.0152	2.33×10^{-20}	7.40×10^{17}	0.0172	0.0173
305-315	0.0239	3.68×10^{-20}	1.09×10^{19}	0.401	0.418
315-325	0.0315	4.86×10^{-20}	2.74×10^{19}	1.33	1.75
325-335	0.0359	5.53×10^{-20}	4.98×10^{19}	2.75	4.50
335-345	0.0359	5.53×10^{-20}	5.49×10^{19}	3.04	7.54
345-355	0.0348	5.35×10^{-20}	6.28×10^{19}	3.36	10.90
355-365	0.0221	3.41×10^{-20}	6.49×10^{19}	2.21	13.11
365-375	0.0168	2.58×10^{-20}	8.09×10^{19}	2.09	15.20
375-385	0.0071	1.09×10^{-20}	7.43×10^{19}	0.810	16.01
385-395	0.0037	5.8×10^{-21}	8.12×10^{19}	0.471	16.48
395-405	0.0009	1.4×10^{-21}	1.11×10^{20}	0.155	16.64
405-415	0.0007	1.1×10^{-21}	1.41×10^{20}	0.155	16.80
415-425	0.0000	0	1.47×10^{20}	0.000	16.80
				Photolysis Rate = 16.8 day^{-1}	

*6.52×10^{16} molecule cm^{-3} in 9.98 cm pathlength cell.

$A_{\Delta\lambda blank}$ = 0.0001. The sample trace also lay at -0.0001 absorbance units relative to a zero point at 450 nm. The absolute absorbance is therefore $A_{\Delta\lambda sample}^{corr}$ = 0.0001 + 0.0001 + 0.0149 = 0.0151 in base 10 units. Thus, in logarithm base e units , $A_{\Delta\lambda sample}^{corr}$ = 0.0348 ($345 \leq \lambda \leq 355$ nm). Since l = 9.98 cm, the cross section, from the Beer-Lambert Law, is

$$\sigma_{\Delta\lambda} = \sigma_{350} = \frac{0.0348A}{(6.52 \times 10^{16} \text{ molecule cm}^{-3})(9.98 \text{ cm})}$$

$$= 5.35 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$$

The component of k_p^{max} for this wavelength interval is

$$k_{p350}^{max} = J_{350}\sigma_{350}$$

$$= (5.35 \times 10^{-20} \text{ cm}^2)(6.28 \times 10^{19} \text{ photons cm}^{-2} \text{ day}^{-1})$$

$$= 3.36 \text{ day}^{-1}$$

By summing the components of k_p^{max} for each wavelength interval listed in Tables 1, 2 and 3, k_p^{max} for the desired latitude and time of year may be determined. Table 4 illustrates this process for the acrolein spectrum of Figure 4.

5. Information to be Reported

A report of the results of the tests must include the following:

(1) The compound name, formula, structure and the chemical form used, including any impurities.

(2) The method used, vapor or solution.

(3) The range of sample concentrations studied and cell length.

(4) The mean, standard deviation and number of runs. If a single low pressure value was used, a justification shall be provided.

(5) For solution phase results, the two solvents and their respective k_p^{max} values.

(6) Absorption spectra and the wavelength averaged values of $\sigma_{\Delta\lambda}$ so derived.

(7) The apparent photochemical rate constants, k_p^{max} ($days^{-1}$), at 10^o, 30^o and 50^oN for the summer and winter solstices, and the equinox.

(8) Anything unusual about the test.

(9) Any other relevant information.

REFERENCES

Atkinson, R. and A. C. Lloyd, 1980. Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog. Final Report to EPA Contract No. 68-02-3280, Environmental Research and Technology, Inc. Document No. P-A040, Westlake Village, CA.

Finlayson-Pitts, B. J. and J. N. Pitts, Jr. 1977. The chemical basis of air quality: Kinetics and mechanisms of photochemical air pollution and application to control strategies. Adv. Environ. Sci. Technol., 7,75.

Herron, J. T., R. E. Huie and J. A. Hodgeson (Eds.). 1979. Chemical Kinetic Data Needs for Modeling the Lower Troposphere. National Bureau of Standards Special Publication 557, August.

Demerjian, K. L., K. L. Schere and J. T. Peterson. 1980. Theoretical Estimates of Actinic (Spherically Integrated) Flux and Photolytic Rate Constants of Atmospheric Species in the Lower Troposphere. Adv. Environ. Sci. Technol., 10, 369.

Peterson, J. T. 1976. Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Applications. EPA-600/4-76-025, June.

Calvert, J. G. and J. N. Pitts, Jr. 1966. "Photochemistry," Wiley, New York, NY.

Benson, S. W. 1976. "Thermochemical Kinetics," 2nd Ed., Wiley-Interscience, New York, NY.

Pitts, J. N. Jr., A. M. Winer, D. R. Fitz, S. M. Aschmann and R. Atkinson. 1981a. Experimental protocol for Determining Ozone Reaction Rate Constants. EPA-600/S3-81-024, May.

Pitts, J. N. Jr., A. M. Winer, D. R. Fitz, M. C. Dodd, S. M. Aschmann and R. Atkinson. 1981b. Experimental Protocol for Determining Hydroxyl Radical Rate Constants. Report in preparation.

Hendry, D. G. and R. A. Kenley. 1979. Atmospheric Reaction Products of Organic Compounds. EPA-500/12-79-001, June.